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LETTERS TO THE EDITOR

Dedicated to B.I. Buzykin on His 80th Anniversary

Synthesis and Structure of a Copper(II) Complex of *N,N'*-Bis(di-*para*-tolylphosphinoylmethyl)-1,8-diamino-3,6-dioxaoctane

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Abstract—A copper(II) complex of *N,N'*-bis(di-*para*-tolylphosphinoylmethyl)-1,8-diamino-3,6-dioxaoctane was synthesized and its crystal structure was established. The inner coordination sphere of the complex is a strongly distorted trigonal bipyramid. Coordination involves the phosphoryl oxygen atoms, nitrogen atoms, and ether oxygen atom, and one axial position is occupied by a water molecule.

Keywords: phosphorylated diazapodands, copper complex, crystal structure
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Neutral α-aminophosphoryl compounds present a high interest as efficient extractants for hydrometallurgical processes and reagents for analytical chemistry [1–7]. Functionalized derivatives of these compounds, in particular, phosphorylated azapodands, have shown high efficiency and selectivity as carriers capable of transporting alkali and alkaline-earth and some other metal cations through hydrophobic membranes in membrane extraction processes [8, 9].

To gain insight into the nature of the compounds formed in extraction systems and transported from the feed to receiving phase, we considered it necessary to assess the crystal and molecular structure of metal complexes of phosphorylated azapodands. We could synthesize a copper(II) complex of one of the bisphosphorylated azapodands, specifically, *N,N'*-bis-(di-*para*-tolylphosphinoylmethyl)-1,8-diamino-3,6-dioxaoctane, which we synthesized in [10]. The synthesis was performed by the reaction of the podand with copper nitrate in a methanol solution. Note that in the present paper we for the first time report comprehensive structural characterization of the used podand (Scheme 1).

The starting *N,N'*-bis(di-*para*-tolylphosphinoylmethyl)-1,8-diamino-3,6-dioxaoctane is a potential hexadentate ligand capable of coordinating to metal ions via its ether and phosphoryl oxygen atoms, as well as nitrogen atoms. However, the dentacity of the ligand in the isolated copper complex proved to be equal to 5. Coordination involves two phosphoryl oxygens, two nitrogens, and one ether oxygen, while the sixth coordination site is occupied by a water molecule (Fig. 1).

The copper ion has a strongly distorted octahedral configuration. The equatorial plane accommodates two nitrogen atoms, one phosphoryl oxygen atom, and a water molecule. One phosphoryl oxygen and one ether oxygen are in axial positions; the O^2CuO^{22} angle between these oxygens is 158°, and they are quite remote from the copper ion (2.42 and 2.57 Å). The lengths of the equatorial coordination bonds are typical for those with copper ions (1.95–2.06 Å). We suggest that the distortion of the coordination geometry of copper is due to the strain of the formed five-membered rings, as well as by the weak additional interaction between the copper atom and the O^{19} ester oxygen atom; Cu–O distance 3.1 Å. This short contact